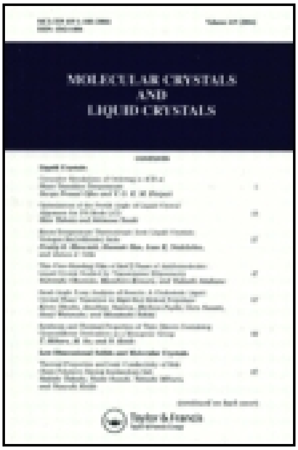

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Magnetic Susceptibility Studies on a Lyotropic Liquid Crystal System - The Role of Bound Water

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Magnetic Susceptibility Studies on a Lyotropic Liquid Crystal System – The Role of Bound Water

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The bound water in aqueous micellar systems like the Cesium perfluoroprooctanoate (CsPFO)/water has been extensively studied using molecular simulations. However, suitable experimental techniques to probe the bound water (hydrogen bonded water molecules to the micellar surface) in these systems are lacking, as the hydration layer is very thin. The free or bulk water magnetic susceptibility is related to the number of hydrogen bonds between the water molecules. Hence, one can employ the magnetic susceptibility studies to probe the bound water effectively when the micellar aggregation number is small. With this view, we have carried out magnetic susceptibility studies on CsPFO/water system in the isotropic phase for various concentrations. We find that the susceptibility increases with decrease in temperature, exhibits a maximum and then decreases linearly. The decrease in susceptibility with decrease in temperature below the maximum can be related to the aggregation number of the micelles. On the other hand, the increasing trend in the susceptibility at higher temperatures (where the aggregation number of the micelles is small) may be attributed to the bound water. Further, we find that with decreasing concentration of CsPFO, the susceptibility maximum shifts towards the low temperature side indicating that the bound water extends to lower temperatures. From our magnetic studies, we infer that at very low concentrations of CsPFO (<15 wt%), the bound water can be present even at room temperature. This is in agreement with the reported molecular simulation studies carried out for the same concentration of CsPFO.

Keywords: bound water; lyotropic liquid crystal; magnetic susceptibility; micelles

1. INTRODUCTION

The structure and dynamics of water in the vicinity of biological macromolecules or micellar aggregates in aqueous solutions are reported to be different from the bulk water. Many theoretical and

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experimental investigations are reported on the bound water associated with micellar and biological systems [1]. The experimental studies mainly involve the dielectric relaxation, solvation dynamics and neutron scattering techniques [1,2]. Dielectric relaxation is not a sensitive probe to study the bound water as it measures the collective response of the entire system, namely, the rotational reorientation of the biological molecule, bound water and free water. In the solvation dynamics, the studies depend on the correct positioning of the probe molecules in the stern layer, which is subject to error due to the partial diffusion of the probe molecules into the bulk or into the hydrocarbon region. A better technique would be to probe the presence of bound water by measuring the magnetic susceptibility of the system. The free or bulk water magnetic susceptibility is related to the number of hydrogen bonds between the water molecules [3]. Stefanov and Saupe have reported the magnetic susceptibility measurements on a nematic liquid crystal consisting of decylammonium chloride/ammonium chloride/ water. They attributed the susceptibility in the isotropic phase to the mass diamagnetic susceptibility of bulk water arising due to the temperature dependence of the number of hydrogen bonds between water molecules [4]. Since the water molecules in the vicinity of the macromolecules (or micellar aggregates) are hydrogen bonded to the head groups, we believe that magnetic susceptibility studies can be employed to study the bound water in these systems. Molecular simulation studies have been reported for CsPFO/water micellar system for a low aggregation number, which predicted bound water in this system [5,6].

Cesium perfluorooctanoate/water liquid crystal is a well studied system [7–10]. This system exhibits isotropic, nematic and lamellar phases on cooling for a range of concentrations. Holmes *et al.*, reported the temperature and concentration dependence of the average aggregation number or the size of the micelles covering all the isotropic, nematic and lamellar phases through x-ray studies [10]. They observed that for a given temperature, the aggregation number initially increases with concentration, reaches a maximum and then decrease. They also found that for a given concentration of CsPFO, the aggregation number increases with decrease in temperature. We have reported recently our preliminary magnetic susceptibility studies on CsPFO/water system for different concentrations covering the isotropic and nematic phases [11]. Combining the results of Holmes *et al.*, with our results on concentration and temperature dependence of magnetic susceptibility, we inferred the susceptibility to be inversely related to the aggregation number. According to Holmes *et al.*, the aggregation number increases with decrease in temperature for a given concentration.

Consequently, the susceptibility for a given concentration can be expected to decrease with decrease in temperature. This trend is seen in the low temperature regime of the isotropic phases of 40%, 45% and 50% concentrations of CsPFO in water. However, for 55% CsPFO in water, the susceptibility in the isotropic phase is found to increase weakly with decrease in temperature. We suggested that this discrepancy in the susceptibility at a high concentration of CsPFO may be related to the presence of bound water in the system, since the aggregation number of the micelles are reported to be low in this temperature-concentration regime [11]. To probe this aspect further, we extended out magnetic susceptibility studies to higher temperatures (the regions of low aggregation numbers) of the isotropic phases of 40%, 45% and 50% concentrations of CsPFO in water. Interestingly, in these concentrations also, in the high temperature regime, we find an increase in susceptibility with decrease in temperature. On decreasing the temperature further, we find the susceptibility exhibits a maximum and then decreases. We infer that the susceptibility and its temperature dependence are related to the bound water in the higher temperature regime (above the maximum) and to the aggregation number in the lower temperature regime.

2. EXPERIMENTAL

We used the lyotropic liquid crystal system CsPFO dissolved in deionised millipore water. The measurements were carried out for four different concentrations of CsPFO namely, $CsPFO/H_2O = 40/60$ wt % (sample A), $CsPFO/H_2O = 45/55$ wt % (sample B), $CsPFO/H_2O = 50/50$ wt % (sample C) and $CsPFO/H_2O = 55/45$ wt % (sample D). The isotropic-nematic transition temperatures (T_{IN}) were 309 K, 312 K, 320 K and 330.6 K for the samples A, B, C and D respectively. For the susceptibility measurements, oxygen was removed from the Millipore water by bubbling dry nitrogen gas through it for several hours.

The material CsPFO was added to this water under a nitrogen atmosphere and the components were mixed thoroughly. Typically about 5.2 mg of the sample was taken in a Perkin Elmer DSC sample cup and sealed to prevent evaporation of water using standard procedures.

We used a Faraday balance (Oxford Instruments) to measure the susceptibility as a function of temperature. The details of our experimental set up and the measurement of the sample susceptibility is given elsewhere [11]. The susceptibility measurements were carried out while cooling the sample from high temperatures.

3. RESULTS AND DISCUSSION

The mass diamagnetic susceptibility as a function of temperature for four different concentrations of CsPFO in water is shown in Figure 1. For 40%, 45% and 50%, the susceptibility in the isotropic phase initially increases with decrease in temperature and exhibits a maximum and then decreases. However, for 55% CsPFO, we find only an increase in susceptibility in the isotropic phase with decrease in temperature. The absence of the susceptibility maximum for 55% CsPFO may be related to the occurrence of isotropic-nematic transition (T_{IN}) at a relatively high temperature for this concentration. For lower concentrations, the maximum shifts towards lower temperatures with decreasing concentration. Recently reported molecular simulation studies on this system at very low aggregation number (60) suggest the presence of bound water (water molecules hydrogen

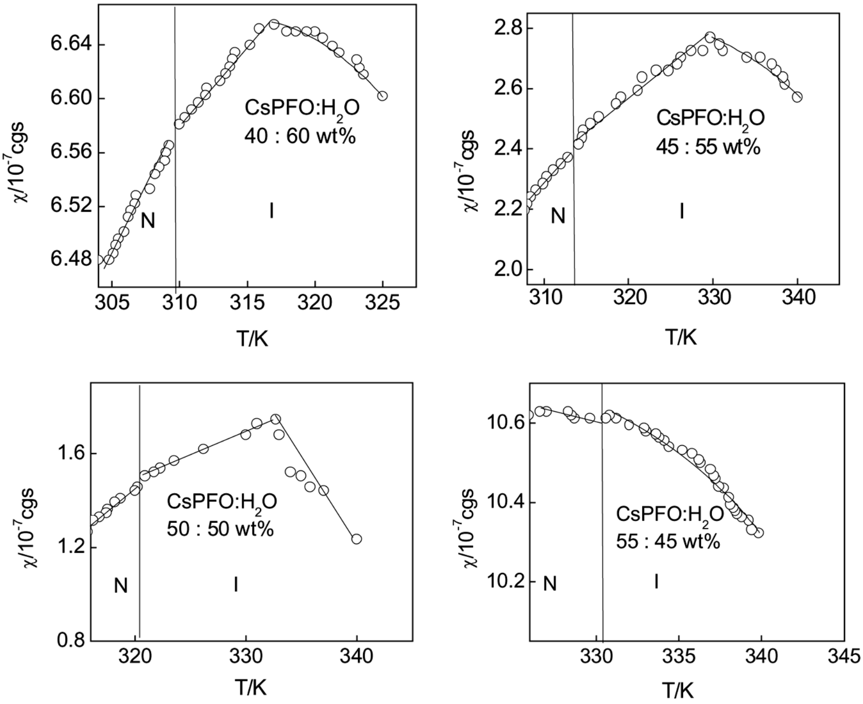

FIGURE 1 The mass diamagnetic susceptibility as a function of temperature for four different concentrations of CsPFO in water. The maximum shifts towards lower temperatures with decreasing concentrations of CsPFO in water.

bonded to the micellar surface) [6]. Interestingly, in the region where we find the increase in susceptibility with decrease in temperature (in the isotropic phase), the aggregation number is expected to be low and nearly of the same order used in the simulation [10]. Further, the susceptibility is expected to decrease with decrease in temperature if it is related to the aggregation number [11].

This suggests that in the high temperature regime, the observed susceptibility and its temperature dependence is related to that of the bound water. Further, it is known that the temperature dependence of susceptibility on bulk or free water is inversely related to the number of hydrogen bonds between the water molecules [3]. Hence, we believe that, the increase in susceptibility with decrease in temperature in the high temperature regime in our system is related to the decrease in the number of hydrogen bonds between the water molecules and the micellar surface. Consequently, the observed maximum in the susceptibility may indicate the temperature above which the bound water is dominant and below which it is negligible. We find that the susceptibility maximum shifts towards the lower temperatures when we decrease the concentration of CsPFO. For example, the temperature at which the susceptibility maximum occurs are 336 K, 330 K and 317 K for 50%, 45% and 40% CsPFO respectively. This trend indicates that the maximum may even shift to 300 K for a lower concentration of CsPFO. This suggests that the bound water can exist even at 300 K. This is in agreement with the simulation studies carried out at very low concentration of CsPFO (15 wt%) in water in which the authors predict bound water at 300 K [6]. However, our results do not agree with their predictions of temperature dependence of bound water. Their results show that the bound water is dominant at 300 K than at 350 K. This discrepancy with the simulation studies can be due to the authors neglecting the increase of the aggregation number at 300 K with respect to that at 350 K. We therefore infer that in the high temperature regime (above the maximum), the observed susceptibility is related to the bound water and in the low temperature regime (below the maximum), it is related to the aggregation number of the micelles. Recently, another simulation study investigating the interaction between ionic surfactant (sodium dodecylsulfate) layers with thin water films has been reported [12]. The authors predicted a short range, strong repulsive force between ionic surfactant layers induced by the layers of highly polarized water (bound water). Accordingly, we can assume that the bound water in our system on the micellar surfaces is likely to exert some repulsive hydration force between the micelles. This repulsive force may be responsible in preventing the large aggregation of micelles at the high temperature regime.

4. CONCLUSIONS

We have carried out magnetic susceptibility studies on four different concentrations of CsPFO in water. We find that the susceptibility increases with decrease in temperature in the high temperature regime (above the maximum) and decreases with decrease in temperature in the low temperature regime. We analyze our results by comparing with the simulation studies carried out on the same system and suggest that the susceptibility variation at high temperature regime is dominated by the presence of bound water and at low temperature regime, it is dominated by the aggregation number.

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